

AD-A194 583 NEW SYNTHETIC APPROACHES TO IOT(U) BROWN UNIV (GERMANY F 1/1  
R) H MANNHOFF 01 OCT 85 DAJA45-85-C-0016

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INSTITUT FÜR ORGANISCHE CHEMIE  
UND BIOCHEMIE  
DER UNIVERSITÄT BONN  
Prof. Dr. H. Wamhoff

Gerhard-Domagk-Straße 1  
D - 5300 Bonn 1, 1. OG. 1088  
Tel. (0228) 731  
Bei Durchwahl 732651, 732671  
Telex 886657 unibo d

(2)

European Research Office  
Chemistry Branch  
Attn: Fiscal Officer  
USARSG-UK Edison House  
223 Old Marylebone Road  
GB - London NW1 5TH ENGLAND

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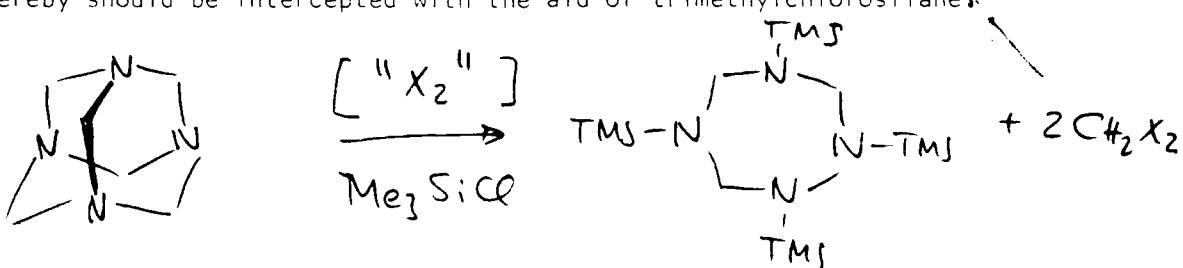
Ref: Contract No. DAJA 45-85-C-0016  
"New Synthetic Approaches to TAT"

## SECOND INTERIM REPORT (Item 0002)

After in the First Interim Report has been stated that the research work on the above named project has been started on July 1, 1985, this second interim report deals with the additional informations and first experiments carried out in the meantime.

Mr. Dipl.-Chem. Marcus Bongen has been appointed meanwhile to be the second researcher in this project besides Mr. Dipl.-Chem. Johannes Nagelschmitz.

Mr. Bongen will try within this project other promising approaches to the synthesis of TAT. One approach is the partial degradation of urotropine (hexamethylene-tetramine) with the aid of halogenating agents (i.e. the selective removal of two CH<sub>2</sub>-bridges being transformed into CH<sub>2</sub>X<sub>2</sub>). The monocyclic tetrazocane formed thereby should be intercepted with the aid of trimethylchlorosilanes.



Reactive agents ("X<sub>2</sub>") which might be employed:

$\text{PPh}_3/\text{CCl}_4 \rightarrow \text{Ph}_3\text{P}(\text{O})\text{Cl}_2 \dots \text{CCl}_3$

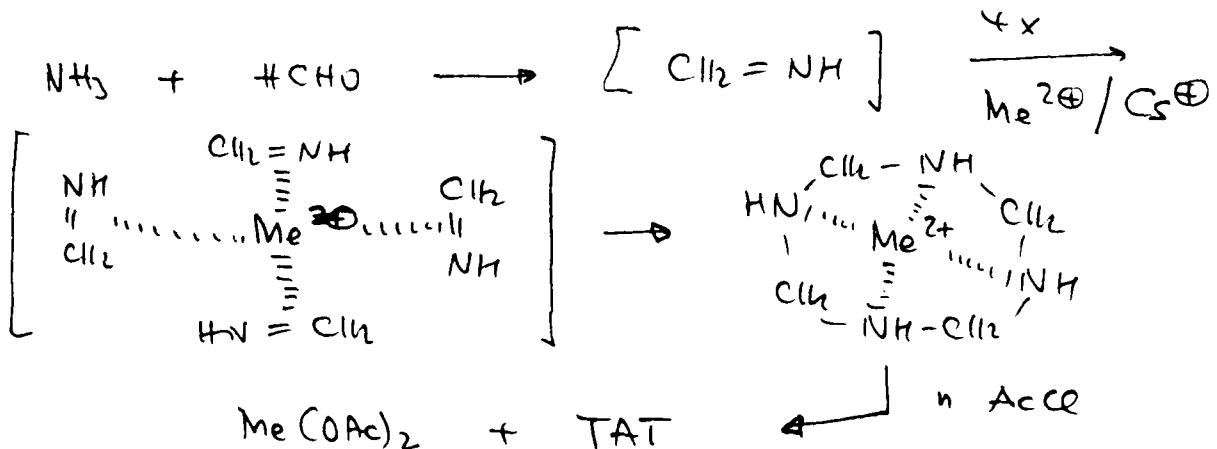
$\text{PPh}_3/\text{C}_2\text{Cl}_6 \rightarrow \text{Ph}_3\text{PCl}_2$

$\text{POCl}_3$

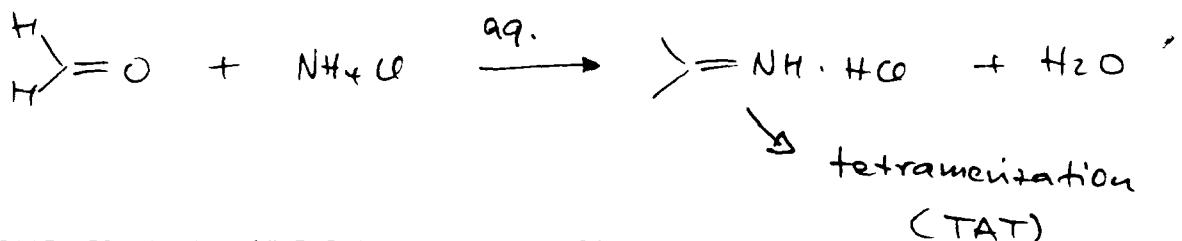
$\text{PX}_5 \quad \text{Ph}_2\text{PBr}_3$

This approach combines the classical urotropine synthesis from simple commercial compounds, like formaldehyde and ammonia with the subsequent selective removal of two methylene bridging units, leading to a monocyclic 8-membered tetrazocane derivative. This approach might surpass the known procedure of Wang Shaofeng and Fu-ping, cf. Chem. Abstr. 97 (1982) 130 024.

Furthermore, Mr. Bongen will try to modify the classical hexamethylenetetramine synthesis in the presence of several complexing transition metal ions, like  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  (with the assistance of the Cs-Effect), i.e. under typical template conditions:

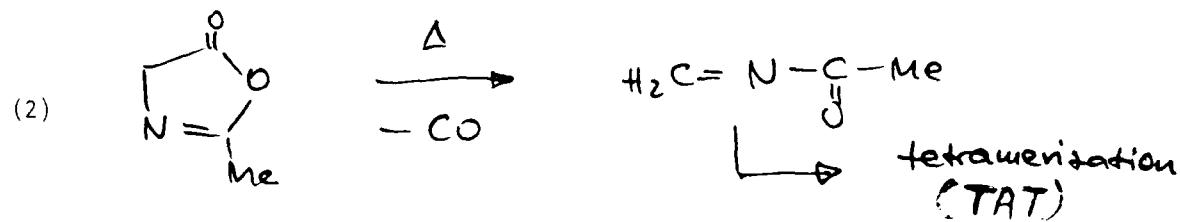
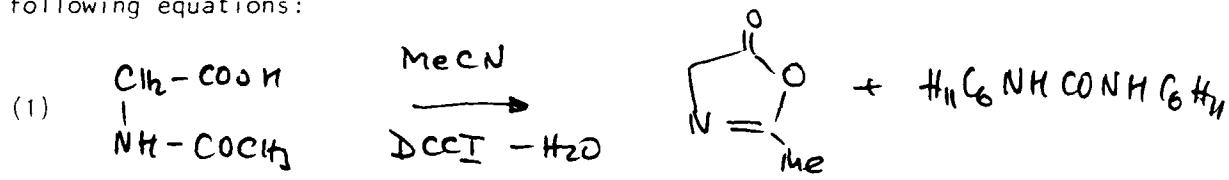


Finally, Mr. Bongen will try the classical approach, as mentioned in the First Interim Report (according to Werner, J.Chem.Soc. 1917, 844):



## BRIEF DESCRIPTION OF THE FIRST EXPERIMENTS:

Mr. Nagelschmitz is at present involved to work out a reliable synthesis (1) of 2-methylazlactone, which is a powerful precursor for thermal (pyrolytic) decarbonylation (2) to afford eventually acetyl-methyleneimine, according to the following equations:



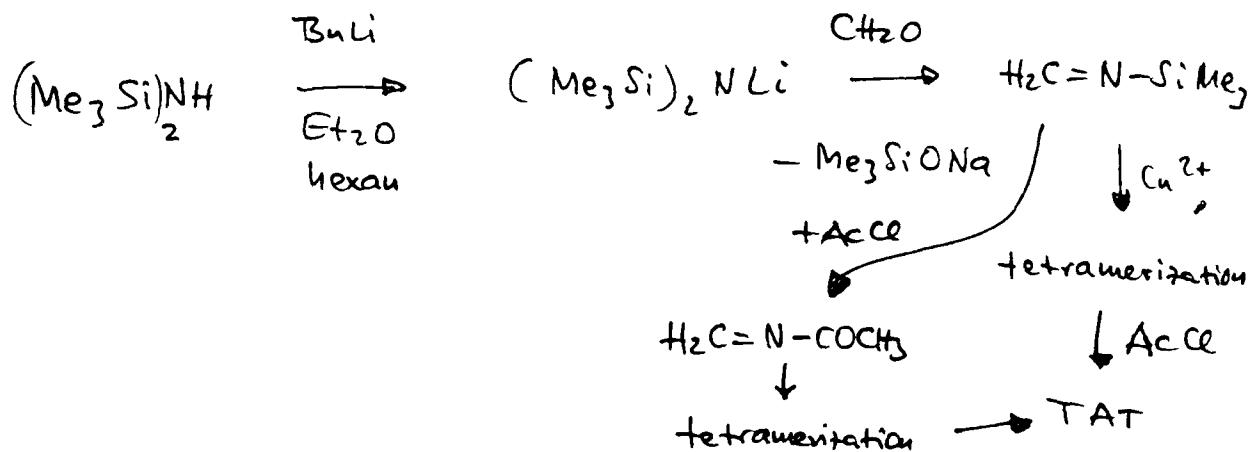
All experiments carried out so far, show that the azlactone is readily formed, but the working-up and purification procedures have turned out to be rather problematic, due to a high sensitivity of the azlactone again heat and moisture. One special problem is the separation of the dicyclohexylurea formed during the cyclocondensation step. The azlactone proves to be highly thermally unstable at temperatures  $>40^{\circ}\text{C}$ .

Treatment of the acylated amino acid in (1) with  $\text{Ph}_3\text{PCl}_2$  made insitu from  $\text{PPh}_3$  and  $\text{C}_2\text{Cl}_6$  and following chromatography under inert conditions could be advantageous:

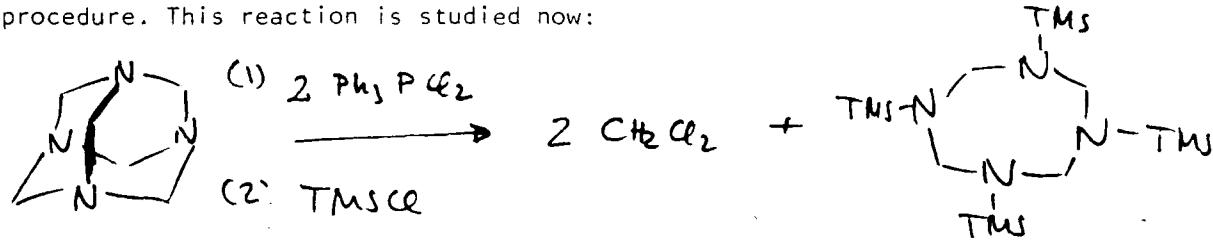


If the azlactone cannot be isolated in pure state it is planned to employ the crude product directly in thermolysis reactions.

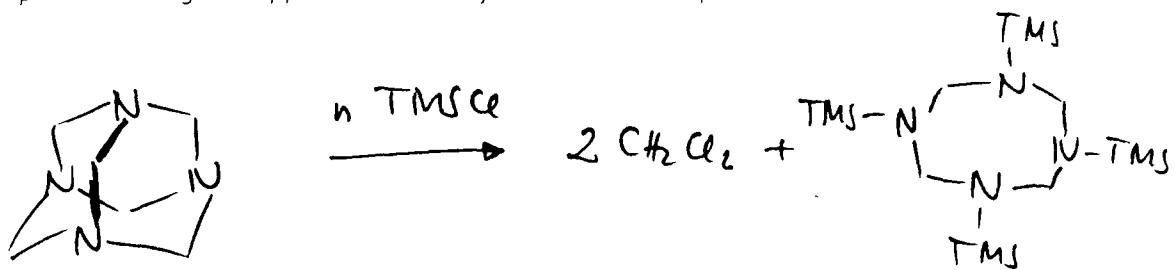
Under current investigation is also the lithiation of silylated ammonia, subsequent treatment with formaldehyde, and exchange of the silyl group by acylation. The methyleneimines formed primary are tried to tetramerize upon treatment with transition metal ions, as shown below:



Mr. Bongens first experiments have shown the following results: The complex  $\text{Ph}_3\text{P} \cdots \text{Cl} \cdots \text{CCl}_3$  generated *in situ* from  $\text{PPh}_3$  and  $\text{CCL}_4$  ("Appel-reaction") has proved to be too weak for degradation of the urotropine molecule. After mutual treatment of hexamethylenetetramine with this reagent and trimethylchlorosilane (as interception agent) the unchanged starting material was recovered. However, employing dichlorotriphenylphosphorane or its bromo analog, possessing both a much higher halogenating potential should result in a much more promising procedure. This reaction is studied now:



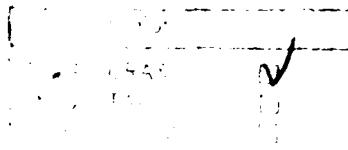
Currently is also investigated a long time treatment of urotropine in TMSCl, acting both as solvent and reactant. If the potential of TMSCl is sufficient, a simple and elegant approach to silylated TAT is opened:



From urotropine was obtained in the system  $\text{POCl}_3/\text{CH}_2\text{Cl}_2/\text{TMSCl}$  was obtained a novel substance (mp 139-142°C; water soluble, not sublimable, develops  $\text{NH}_3$  with NaOH). Similarly treatment of urotropine with  $\text{PH}_3\text{PBr}_2$  affords in  $\text{CH}_2\text{Cl}_2$ -solution another solid compound (mp 183-185°C; water soluble, not sublimable, develops  $\text{NH}_3$  with aq. NaOH).

The elucidation of the constitutions of both products is under investigation now.

  
(Prof. Dr. H. Wamhoff)



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